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2. Preparation of R^3-M ($M = MgCl, Cu, Cu_3Li_3, Ag, Ag_3Li_3, ZnCl$ or Zn_3)

The R^3-M compounds shown in Tables I and II were obtained by adding an appropriate amount of $MgCl_2, CuBr, AgBr(LiBr)_3$ or $ZnCl_2$, respectively to R^3-Li (0.020 mole) in THF at $-20^\circ C$ (see under 1). Stirring at this temperature was continued for 15 min.

Vinylzinc chloride (0.020 mole) was obtained by stirring a solution of $H_2C=CH-MgBr$ (0.020 mole) with $ZnCl_2$ (0.020 mole) for 30 min at $0^\circ C$ in THF (40 ml). The zinc compound $HC\equiv C-ZnCl$ (0.020 mole) was prepared by stirring, $HC\equiv C-MgCl$ (0.020 mole) with $ZnCl_2$ (0.020 mole) at $25^\circ C$, in THF (40 ml). The resulting solutions were used as such.

3. General procedure for the conversion of 1 and 4 into 2

To a stirred solution of R^3-M (0.020 mole: $M = Li, MgCl, Cu, Ag$ or $ZnCl$; 0.010 mole: $M = Cu_3Li_3, Ag_3Li_3$ or Zn_3) in THF (40 ml: $R^3 \neq HC\equiv C-C\equiv C-$; 120 ml: $R^3 = HC\equiv C-C\equiv C-$) were subsequently added, at $-20^\circ C$, $Pd[PPh_3]_4$ (0.02 M solution in THF; for amounts see Tables I and II) and substrates 1 (0.020 mole) or 4 (0.020 mole). Stirring of the resulting mixture was

continued for the periods and at the temperatures indicated in Tables I and II.

The reaction mixture was poured into a saturated aqueous solution of NH_4Cl (containing $NaCN$ (≈ 1 g) when M was Cu, Cu_3Li_3, Ag or Ag_3Li_3). The products were isolated by extraction with pentane (3×75 ml); after washing the combined extracts and drying with $MgSO_4$ the solvent was evaporated *in vacuo*. The residue was distilled; when R^3 was $PhC\equiv C$ or $HC\equiv C-C\equiv C$, purification was performed by column chromatography ($Al_2O_3 + 5\% H_2O$ /hexane). Physical constants and characteristic spectroscopic data for allenes 2 are given in Table III.

Acknowledgements

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Preliminary Communications

A Molecular Cation Channel

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Abstract. A polymer of an isocyanide, $[R-N=C<]_n$, has been synthesized in which R contains a benzo-18-crown-6 group. The crown ether rings are situated on top of each other and form channels which bind metal ions.

In this communication we report on the construction of a synthetic molecular cation channel. This system might serve as a model for a molecular channel in biological membranes¹. The model system is a polymer of an isocyanide. Polymers of isocyanides, called poly(iminomethylenes) or poly(carbonimidoyls), $[R-N=C<]_n$, are prepared from isocyanides by the catalytic action of nickel(II) salts². Their structure is very regular and rigid^{2,3}. The polymer chain is a tightly coiled helix with four repeating units per helical turn (Figure 1). Poly(α -phenylethyl-iminomethylene), 1a, has extensively been studied both by Millich³ and by us^{4,5}. In this polymer the side chains

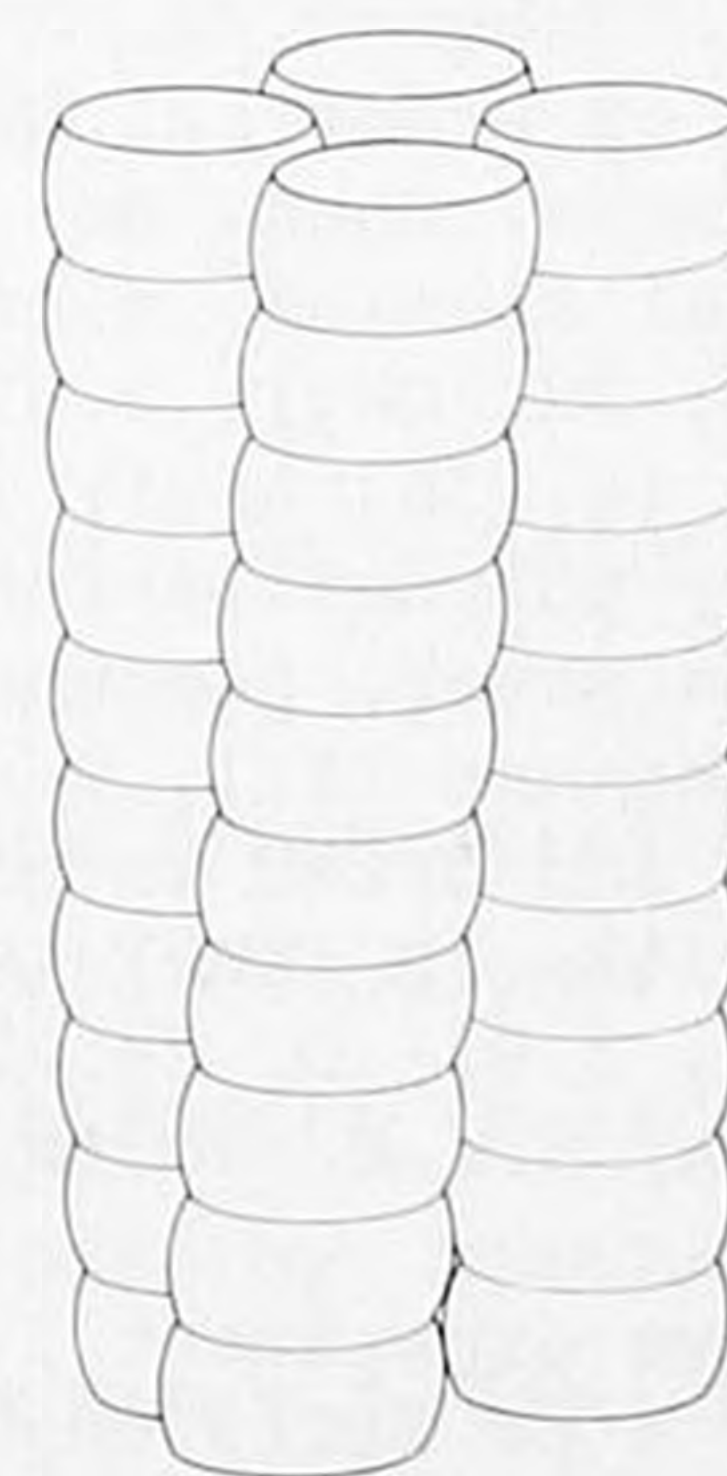
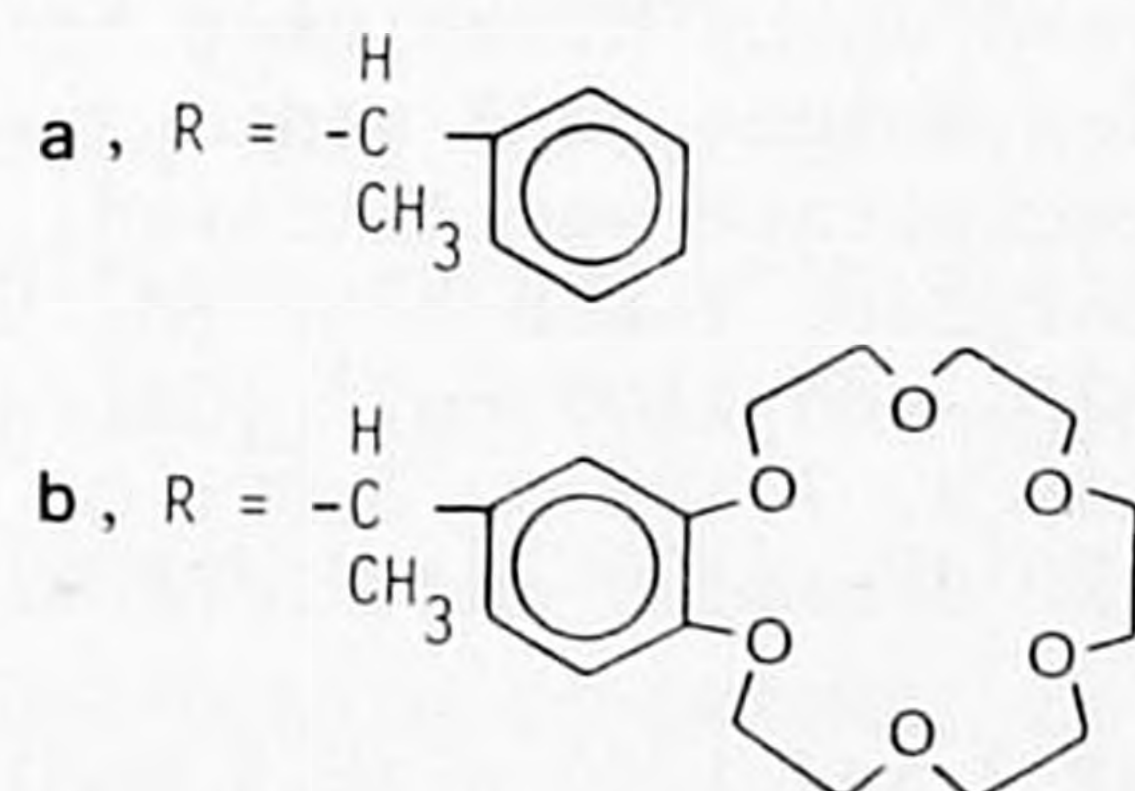
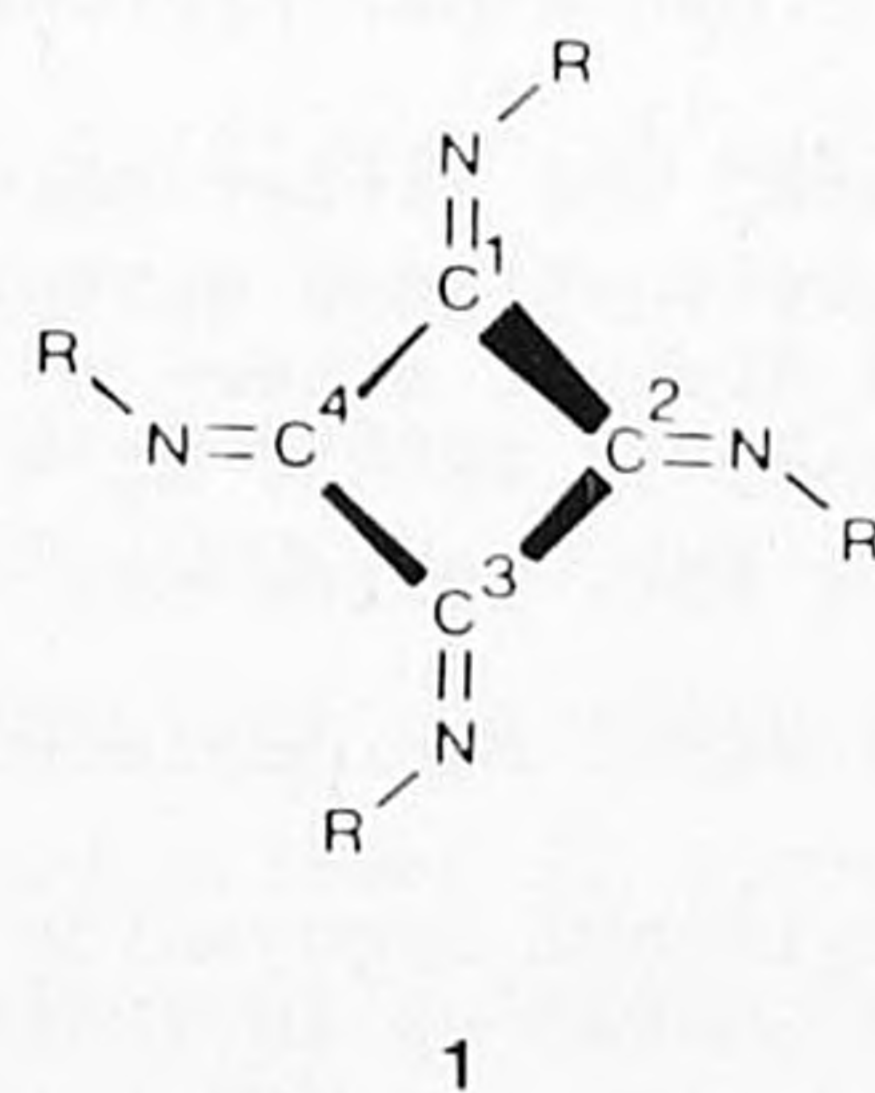
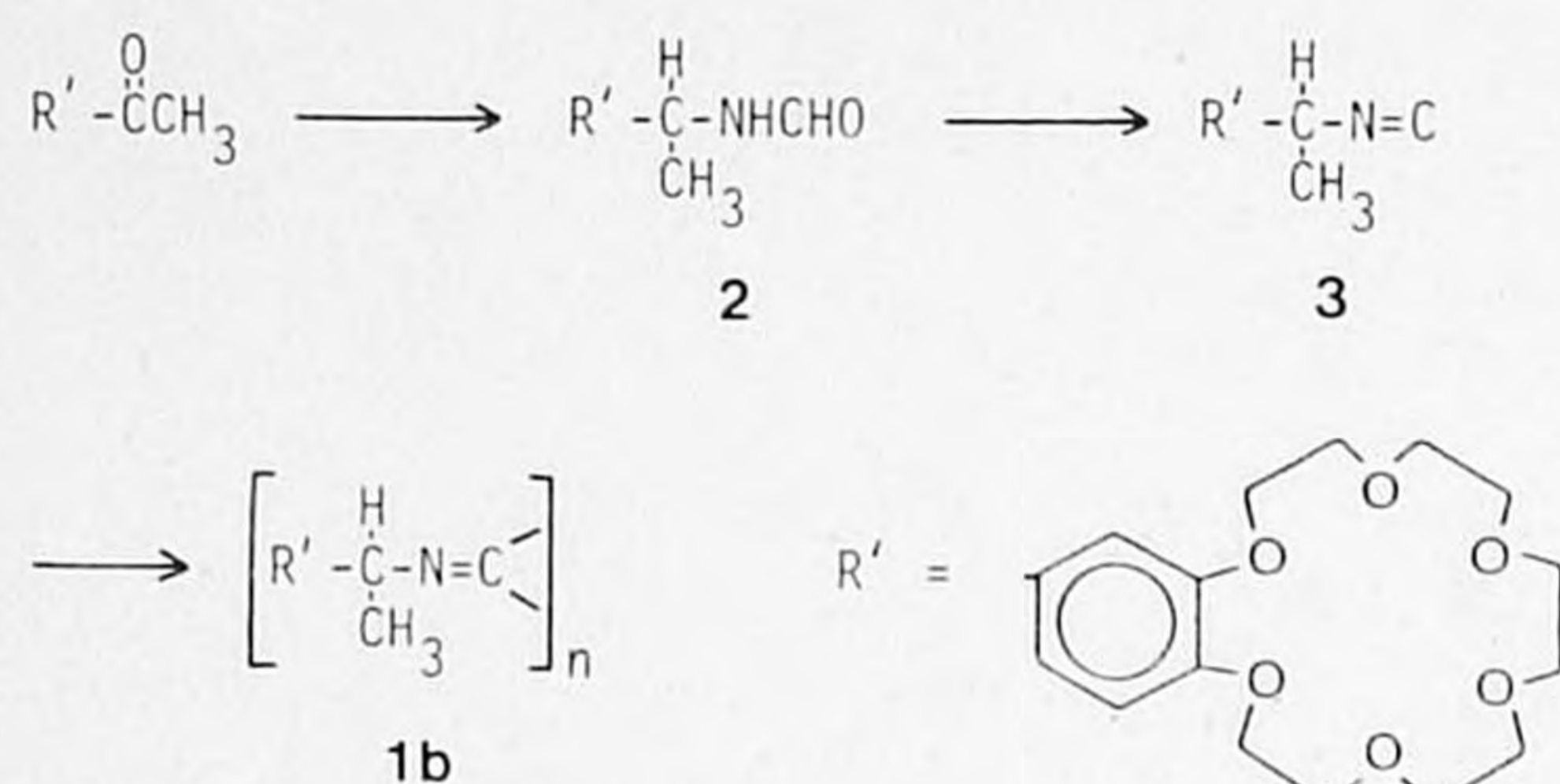


Figure 1. Projection of a poly(iminomethylene) along its helix axis. Repeating unit C^5 is behind C^1 , repeating unit C^6 behind C^2 , etc.

Figure 2. Schematic picture of the four molecular channels.

form four stacks which run parallel to the polymer helix axis. In these stacks the phenyl groups are situated on top of each other and are locked in this position by the tight structure of the polymer chain. If the phenyl groups are part of a crown ether ring system, like in 1b, these crowns are on top of each other and form four channels (Figure 2). Polymer 1b was prepared as shown in Scheme 1. Starting material is 4-acetylbenzo-18-crown-

6 which can be prepared according to literature procedures⁶. The keto function in the latter compound was converted into a formamide group by means of a Leuckart reaction⁷. Formamide **2** was dehydrated with phosphorus oxychloride⁸ and base to give isocyanide **3**. The isocyanide was purified by column chromatography⁹. Polymerization was performed by heating the monomer neat at 90°C for 5 days with 3 mol % of NiCl₂·6H₂O¹⁰. The molecular weight



Scheme 1

of the polymer amounted to $\bar{M}_V = 15,000$, which corresponds to 40 repeating units. Copolymers of α -phenylethyl isocyanide³ and crown ether containing isocyanide **3** were prepared by reacting mixtures of the monomers with NiCl₂·6H₂O at 25-40°C¹².

The binding properties of polymer **1b** and a copolymer¹² of **3** and α -phenylethyl isocyanide towards metal ions and protonated amines were measured by the picrate extraction technique^{6,13}. Representative results are given in Figure 3¹⁴. Reference compounds are 4-acetylbenzo-18-crown-6 and benzo-18-crown-6. The polymers are more effective in extracting cations than the reference compounds. In particular this is true for Rb⁺ and Cs⁺. These ions have large diameters and will be sandwiched between consecutive crown ether rings of the channels. The binding profiles of the homopolymer and the copolymer do not differ greatly. This phenomenon suggests that the copolymer largely is an alternating copolymer in which the crown ether rings are arranged just as in the homopolymer. In other words, the crown ether side chains and the α -phenylethyl side chains are in separate stacks. The amphiphilic nature of polymer **1b** (top and bottom are hydrophilic, outer mantle is lipophilic) makes this compound suitable for incorporation into vesicles, *e.g.* of the type recently prepared from synthetic surfactants¹⁵, and for subsequent ion transport studies. Also, the average chain length of the polymer (4 nm¹⁶) is of the same order of magnitude as the thickness of the bilayers of most vesicles (3 - 5 nm¹⁵).

References and Notes

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9. Woelm W 200 neutral alumina, eluent diethyl ether-ethyl acetate, 1:1 v/v. Yield 80% of colorless oil; ¹H NMR (CDCl₃) δ 1.62 (m, 3H, CH₃); 3.67 (s, 4H), 3.73 (s, 8H), 3.9 (m, 4H), 4.15 (m, 4H), crown ether protons; 4.74 (m, 1H, CH); 6.90 (s, 3H, ArH); IR (neat) 2138 cm⁻¹ (NC), 1260 and 1100 cm⁻¹ (CO).
10. The reddish glassy polymerization product was worked up by dissolving it in chloroform. The latter solution was extracted with water, concentrated to a smaller volume, and added dropwise to a well stirred mixture of diethyl ether-*n*-hexane (1:1, v/v). The flocky precipitate was filtered, washed with diethyl ether-*n*-hexane (1:1, v/v) and dried to give pale yellow polymer. Yield 75%; $[\eta]$ 0.031 (toluene, 30.00°C); $\bar{M}_V = 15,000$ (see Ref. 11); IR (KBr) 1625 cm⁻¹ (N=C), 1260 and 1100 cm⁻¹ (CO). Anal. Calcd. for C₁₉H₂₇NO₆: C, 62.45; H, 7.45; N, 3.83; O, 26.27. Found: C, 62.13; H, 7.19; N, 3.96; O, 26.72.
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12. In a representative experiment 1.3 g (3.5 mmol) of **3** and 1.1 g (8.4 mmol) of α -phenylethyl isocyanide were heated with 3 mol % of NiCl₂·6H₂O at 40°C for 5 days. The polymerization product was worked up as indicated for **1b**. Yield 1.0 g of yellow polymer; $[\eta]$ 0.17 (toluene, 30°C); $\bar{M}_V = 42,000$ (see Ref. 11); IR (KBr) 1625 cm⁻¹ (N=C), 1260 and 1100 cm⁻¹ (CO). Anal. Calcd. for (C₁₉H₂₇NO₆)_{1.72}: C, 70.07; H, 7.24; N, 6.45; O, 16.24. Found C, 70.07; H, 7.17; N, 6.49; O, 16.27.
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14. Association constants of polymer **1b** as measured by the procedure described in Ref. 13, and assuming 1:1 complexes are (picrate, $K_a \times 10^{-5}/\text{mol} \cdot \text{dm}^{-3}$): Li⁺, <5; Na⁺, 20; K⁺, 300; Rb⁺, 120; Cs⁺, 90; NH₄⁺, 55; MeNH₃⁺, 3.4; *t*-BuNH₃⁺, 0.70.
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16. Calculated from the number of repeating units and the distance between these units (0.1 nm, from Ref. 2).

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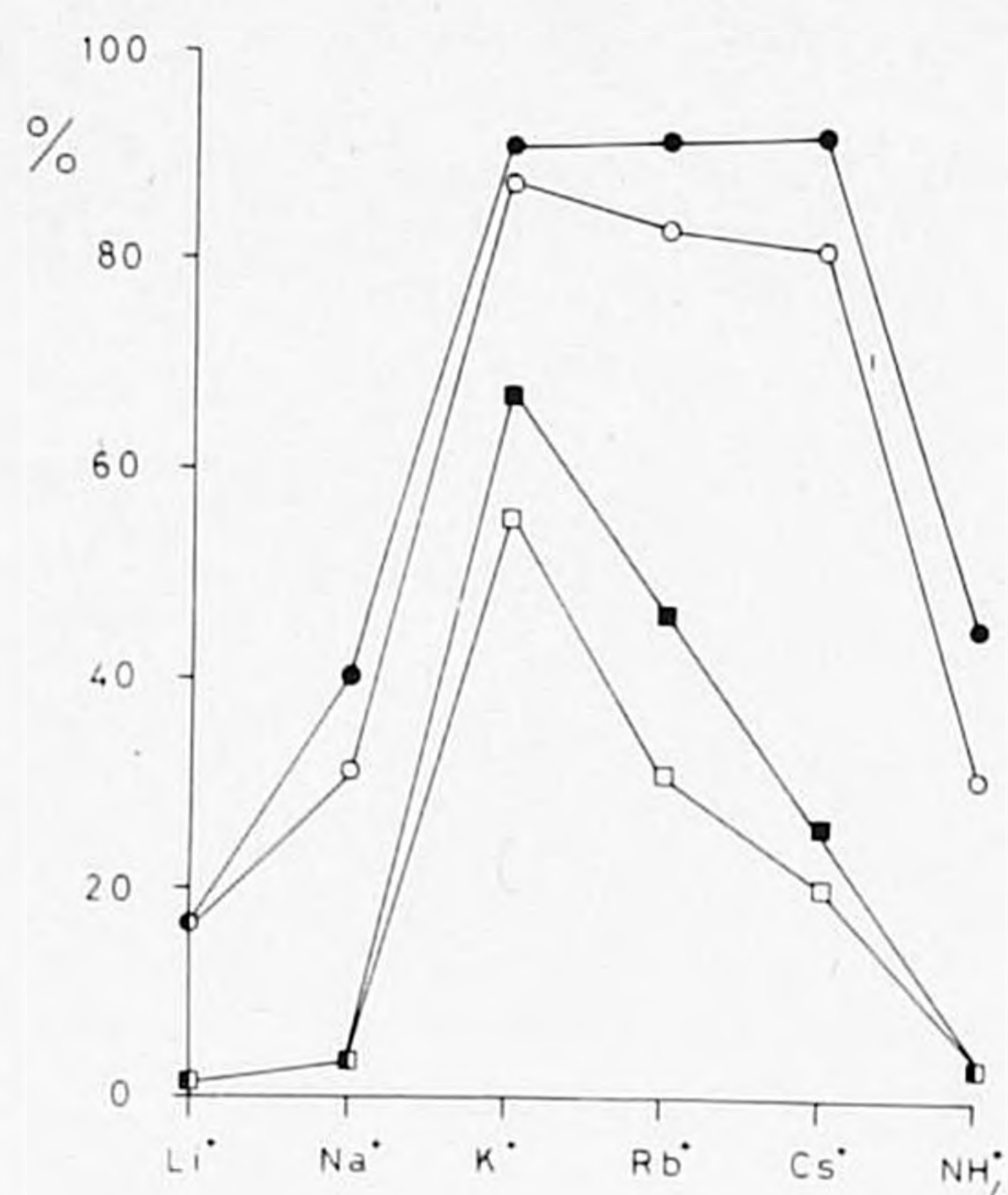


Figure 3. Percentage of picrate salt extracted into the organic layer by polymers and reference compounds. Procedure as described in Ref. 6. Solvent system: H₂O-CH₂Cl₂ (1:1, v/v); [metal picrate] = 1.1 × 10⁻⁴ mol/dm³; [crown ether units] = 5.5 × 10⁻⁵ mol/dm³. (●) Polymer **1b**; (○) 1:1.7-copolymer of **3** and α -phenylethyl isocyanide; (■) 4-acetylbenzo-18-crown-6; (□) benzo-18-crown-6, the data for this compound are taken from Ref. 6